

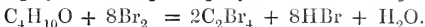
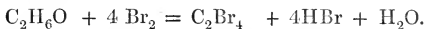


Campbell 2e2
(1-18).

ON THE BROMIDE OF CARBON.

BY ARTHUR E. W. LENNOX.

THE compounds of carbon with bromine have as yet received but limited attention. The tetrabromide of carbon— CBr_4 of the methyl series—is altogether unknown. Kolbe failed in obtaining this compound by submitting disulphide of carbon, at a high temperature, to the action of bromine; and I learn from Dr. Hofmann, that the action of pentabromide of antimony on the disulphide gives no better result. The bromide of carbon C_2Br_4 , has been obtained by Lœwig*, who procured this substance by the action of bromine on alcohol or on ether, when it is formed according to the equations—



These processes appear, however, to be attended with difficulties. At all events, Vœlckel†, who repeated Lœwig's experiments, failed in obtaining the substance described by that chemist.

A simpler method for obtaining this bromide of carbon appeared to present itself in the perfect substitution of bromine for the hydrogen of olefiant gas.

The brominated derivatives of ethylene have been chiefly examined by Regnault and by Cahours, and, more recently, by Wurtz and by Sawitch. The following terms have been obtained :—

Dibromide of ethylene	$\text{C}_2\text{H}_4\text{Br}_2$.
Dibromide of monobrominated ethylene .	$\text{C}_2(\text{H}_3\text{Br})\text{Br}_2$.
Dibromide of dibrominated ethylene .	$\text{C}_2(\text{H}_2\text{Br}_2)\text{Br}_2$.
Dibromide of tribrominated ethylene .	$\text{C}_2(\text{HBr}_3)\text{Br}_2$.
Monobrominated ethylene	$\text{C}_2\text{H}_3\text{Br}$.
Dibromated ethylene	$\text{C}_2\text{H}_2\text{Br}_2$.

It thus appears that the whole series has been obtained, with the exception of the tetrabrominated ethylene, which would be the bromide of carbon obtained by Lœwig in the reaction above indicated.

* Ann. Ch. Pharm., iii, 292.†

† Ibid., xli, 119.

Of the brominated derivatives of ethylene, dibromide of ethylene, monobrominated ethylene (bromide of vinyl), and dibromide of monobrominated ethylene, have as yet been best investigated. In re-examining these substances, in transforming dibromide of ethylene, by the action of an alcoholic solution of potash, into monobrominated ethylene, and the latter, by treatment with bromine, into the corresponding dibromide, I had an opportunity of tracing, step by step, the observations of my predecessors.

The action of an alcoholic solution of potash upon the dibromide of monobrominated ethylene yields, together with secondary products, a comparatively small quantity of the oily compound $C_2H_2Br_2$, which is still further diminished by the extraordinary property exhibited by this substance of undergoing a molecular transformation similar to that of dichlorinated ethylene, as observed by Regnault,* and of monobrominated ethylene, more recently examined by Dr. Hofmann.† Dibrominated ethylene having been lately the subject of a more minute investigation by M. Sawitch,‡ I have not entered upon a more close examination of this body, but have at once, by the renewed action of bromine, converted it into the

Dibromide of Dibrominated Ethylene.

Bromine attacks the dibrominated ethylene with the greatest energy, heat is evolved, and the bromine disappears. When the bromine was no longer fixed, the orange-yellow liquid was treated with a weak solution of potash, washed with water, and ultimately distilled with precaution. It boils at about $200^{\circ}C.$, but not without partial decomposition, white fumes containing hydrobromic acid being given off during ebullition, which powerfully and persistently attacked the eyes.

The bromine-compound is insoluble in water, but dissolves readily in alcohol and in ether; when exposed to a freezing mixture it solidifies to a white crystalline mass. As it was found impossible to purify this substance for analysis by distillation, a current of perfectly dry carbonic acid gas was passed through the liquid heated in a water-bath to about $75^{\circ}C.$ After a time it assumed a lighter colour, and no longer gave off hydrobromic acid.

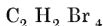
0.470 grm. of substance burnt with lime gave 1.016 grm. of bromide of silver.

* Ann. Ch. Phys. [2.] lxix, 151.

† Chem. Soc. Qu. J., xiii, 68.

‡ Bulletin de la Société Chimique de Paris, 1861, p. 7.

The formula.

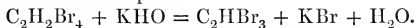


requires the following values.*

	Theory.				Experiment.	
C ₂	..	24	..	„	..	„
H ₂	..	2	..	„	..	„
Br ₄	..	320	..	92.40	..	91.97
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Tribrominated Ethylene.

The dibromide previously described is powerfully acted upon by an alcoholic solution of potash :



Addition of water to the alcoholic solution precipitates the tribrominated ethylene as an oily substance, boiling at 130° C, which, by digestion over chloride of calcium and subsequent careful distillation, may be obtained sufficiently pure for analysis.

0.342 grm. of substance burnt with lime, furnished 0.726 of bromide of silver.

The formula,

C₂HBr₃ requires,

	Theory.				Experiment.	
C ₂	..	24	..	„	..	„
H	..	1	..	„	..	„
Br ₃	..	240	..	90.56	..	90.32
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Tribrominated ethylene, like the other substitution-product of ethylene, is apt to furnish an isomeric solid, which is readily soluble in alcohol and in ether, from which it crystallises in colourless plates. On slowly evaporating a solution of the oily modification in alcohol or ether, the crystalline solid is likewise obtained.

Dibromide of Tribrominated Ethylene.

To obtain this compound, tribrominated ethylene was introduced into a retort, and cautiously distilled into a receiver containing bromine. Combination took place with considerable

* H = 1; O = 16; C = 12; Br. = 80.

evolution of heat. The orange-yellow liquid thus produced was washed with weak potash, and ultimately with water. Thus purified, this bromine-compound is a yellowish red oil, soluble in alcohol and ether, and solidifying when exposed to a frigorific mixture. I have not succeeded in preparing this substance in a state of sufficient purity for analysis; but its nature is sufficiently established by the facility with which it is transformed into tetrabrominated ethylene, or bromide of carbon, by the action of alcoholic solution of potash.

Addition of water to the alcoholic solution precipitates this compound as an oily liquid, which, when slowly deposited by spontaneous evaporation from its solution in alcohol or ether, separates in beautiful crystalline plates of an agreeable aromatic odour and burning taste: one or two crystallisations render it perfectly pure. It is heavier than water; fuses at 50° C; sublimes at a higher temperature; and is not attacked by the mineral acids. These properties identify this compound with the bromide of carbon which Lœwig obtained by the action of bromine upon alcohol and upon ether. For analysis it was dried over sulphuric acid in vacuo, and has furnished the following results.

0.315 grm. of substance burnt with a mixture of oxide of copper and chromate of lead gave 0.078 carbonic acid.

0.175 grm. of substance burnt with lime gave 0.330 grm. of bromide of silver.

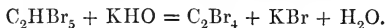
The formula,



requires the following values.

	Theory.			Experiment.		
C ₂	24	..	6.98	6.69.
Br ₄	320	..	93.02	92.57.
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The tetrabrominated ethylene is generated by the action of an alcoholic solution of potash upon the dibromide of tribrominated ethylene, according to the following equation:



The experiments which form the subject of this note were performed in the laboratory of Dr. Hofmann.

